TRANSLATION

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5   To: Mr. Hideo Saito, Governor of Japanese Patent Office

1. Title of the Invention
    Method for the analysis of nitrogen oxide

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SPECIFICATION

1. Title of the Invention

Method for the analysis of nitrogen oxide

2. Patent Claims

A method for the analysis of nitrogen oxide, characterized by using the following procedure.
First, the nitrogen oxide present in the exhaust gas is converted to nitrogen pentoxide and nitric
acid with ozone and then pyrolyzed to form nitrogen dioxide. The nitrogen dioxide is
determined without removing the water present in the exhaust gas through a process not affected
by the water or through a process of further converting the nitrogen dioxide to nitrogen
monoxide, followed by removing the water and then determining the amount of nitrogen oxide
using CLA, NDIR, or electrolysis at constant potential.

3. Detailed Explanation of the Invention

This invention is related to a method for the quantitative analysis of nitrogen oxide (NO_x),
particularly a trace amount of NO_x present in exhaust gas.

NO_x capable of causing air pollution is mainly formed by nitrogen monoxide (NO) and nitrogen
dioxide (NO_2) and can be determined quantitatively with the following methods.

(1) Chemical luminescence assay (CLA)
In this method, NO is oxidized with ozone (O_3) and the NO_2 formed is determined through
chemical luminescence.

(2) Non-diffused infrared spectroscopy (NDIR)
In this method, NO is determined directly through its absorption in the infrared region.

(3) Non-diffused UV spectroscopy (NDUV)
In this method, NO_2 is determined directly through its absorption in the UV region.

(4) Electrolysis at constant potential
In this method, NO and NO_2 are determined in an electrolyte solution by electrolysis.

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(5) Correlated spectroscopy

In this method, accuracy is improved by utilizing absorption at multiple wavelengths. The method has been developed recently and is based on the same mechanism as in Methods (3) and (4).

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When using the methods described above in the analysis of NO_x present in exhaust gas, the result will be affected by the water present in the exhaust gas. Therefore, the water must be removed to a certain degree or the analysis should be carried out on the partially dried exhaust gas.

10 In addition to NO_x, exhaust gas also contains water, SO_2, CO, CO_2, etc., and these components may adversely affect the analysis of NO_x. Particularly, the water present in exhaust gas is able to affect significantly the result obtained from the quantitative analysis of NO_x.

However, when the water is removed, the concentration of NO_x is also decreased.

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The NO_x present in the exhaust gas generated from a furnace, such as boiler, etc., contains mainly NO, which is not very reactive and may not be easily lost during the process of removing water. In other words, the concentration decrease of NO_x is not a serious problem.

20 However, the NO_x present in the exhaust gas generated from a diesel engine or an acid-washing plant may have a high concentration and contains mainly NO_2, which is very reactive and may be easily lost during the process of removing water. In other words, the accuracy of the quantitative analysis of NO_x can be affected significantly.

25 Table 1 shows an example of the results obtained from the quantitative analysis of NO_x. The analysis was carried out for the exhaust gas generated from a diesel engine with PDB (phenol-disulfonic acid) method and CLA method. Significant variation can be observed from the same exhaust gas for the concentration of NO_x obtained with the two methods.

30 Table 1

Conditions	PDB method	CLA method
A	750 ppm	590 ppm
B	890 ppm	770 ppm
C	980 ppm	770 ppm

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Due to the strict regulations on exhaust gas pollution, various measures have been taken regarding exhaust gas released from boilers. As a result, the concentration of NO_x in the exhaust gas is further reduced. On the other hand, however, the concentrations of species with an oxidation state higher than that of NO_2, such as nitrous acid (HNO_2) and nitric acid (HNO_3), may

5   increase. For the two high-oxidation-state species, the current methods for determining the concentration of NO_x described above as well as the related pretreatment methods are not effective.

The purpose of this invention is to solve the problems mentioned above and to provide a method

10   for the quantitative analysis of nitrogen oxide (NO_x), particularly a trace amount of NO_x present in exhaust gas. In the method of this invention, the NO_x present in exhaust gas is first converted to NO_2. The NO_2 is then determined directly or the NO_2 is reduced to NO, which is then determined quantitatively.

15   In the method of this invention, the NO_x present in exhaust gas is first oxidized with O_3 to nitrogen pentoxide (N_2O_5) and nitric acid (HNO_3), which are then pyrolyzed to form NO_2. Next, the NO_2 formed in the exhaust gas is determined quantitatively using a procedure for determining NO_2 not affected by the water present in the exhaust gas, so that the amount of NO_x present in the exhaust gas can be determined. Also, the NO_2 formed in the exhaust gas can be first reduced

20   to NO, followed by dehydration, and then the amount of NO_x present in the exhaust gas can be determined by measuring the amount of NO with a common method, such as CLA, NDIR, or electrolysis at constant potential.

In other words, the NO_x present in exhaust gas is completely converted to NO_2 before the exhaust

25   gas is introduced into the system for quantitative determination of NO_x.

The NO_x present in exhaust gas can be quantitatively determined with the following methods through NO_2 even when the exhaust gas contains water.

30   Since the procedure for quantitative determination of NO_x is not affected by the water present in exhaust gas, for example, the exhaust gas is first introduced into a gas-sealed cell without removing the water. Then, the concentration of NO_x is determined quantitatively using the UV absorption of NO_2. The concentration of NO_x can also be determined quantitatively using ESR.

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Moreover, quantitative determination of NO_x can also be achieved by passing the NO_2-containing exhaust gas through a NO_2-converter capable of converting NO_2 to NO with the CLA method, followed by dehydration and quantitative determination with the CLA method, NDIR method, or electrolysis at constant potential.

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Since the NO_x present in exhaust gas is completely converted to NO_2 before the exhaust gas is introduced into the system for quantitative determination of NO_x, the method of this invention is also suitable for the exhaust gas, which has been treated with other treatment methods recently adopted for exhaust gas. In the method of this invention, the NO_x present in exhaust gas is all

10 converted with any loss. Therefore, a trace amount of NO_x present in exhaust gas can be determined quantitatively at a high accuracy.

The method of this invention can be used for the quantitative determination of NO_x present in exhaust gas generated from a combustion device, such as boiler, heating furnace, gasoline

15 engine, diesel engine, etc., for the quantitative determination of NO_x present in exhaust gas generated from a combustion-type exhaust gas treatment plant, and for the quantitative determination of NO_x present in exhaust gas generated from an iron and steel plant, a chemical plant, etc.

20 In the following, this invention is explained in more detail with practical examples together with the figures attached.

Figure 1 shows the flow chart for the method of this invention. The system for the quantitative determination of NO_x consists of exhaust gas sampling part, O_3 generating part, oxidation

25 reaction part, pyrolysis part, and measurement part.

Exhaust gas sampling part

The NO_x-containing exhaust gas coming from exhaust gas source 1 is sampled through sampling probe 2, dust filter 3, pipeline 4, and pump 5. The gas sample is then sent through pipeline 6 to

30 flow rate regulator 7 and flow meter 8. After the flow rate is adjusted, the gas sample is supplied to oxidation reaction chamber 16.

In order to prevent the problems caused by water condensation from the sample gas, the exhaust gas sampling part should be maintained at a temperature higher than the boiling point of water,

preferably a temperature of 110°C or higher using heating device 22, which consists of a heater and insulating material.

Solid substances, such as ash, etc., are removed through filter 3. Filter 3 can also be installed on the tip of sampling probe 2.

In order to control the gas flow rate, a vent is installed on pipeline 6, so that excess material can be discarded from the system. Flow meter 8 may use various structures, including orifice, etc.

Sampling probe 2, filter 3, pipeline 6, pipeline 9, etc., can be made of stainless steel, quartz, glass, etc.
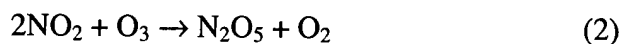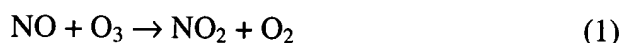
O_3 generating part

A common O_3 generator can be used directly. For example, pure oxygen gas (purity 99.99% or higher) from oxygen tank 10 first passed through flow rate regulator 11 and flow meter 12 and is then sent through pipeline 13 to O_3 generator 14, where O_3 is generated. The O_3-containing oxygen gas is supplied to oxidation reaction chamber 16 through pipeline 15. It should be noted that NO_x may also be formed in O_3 generator 14. Therefore, high-purity oxygen must be used for O_3 generator 14 or the O_3-containing oxygen gas formed must be washed with an alkaline aqueous solution to remove the NO_x through absorption and then dried through a drying agent, such as silica gel, etc.

Oxidation reaction part

In oxidation reaction chamber 16, the sample gas from pipeline 9 and the O_3-containing oxygen gas from pipeline 15 are mixed and the NO_x present in the sample gas is oxidized by O_3.

The oxidation process can be represented by following equations (1) – (5).

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \qquad (2)$$

$$N_2O_3 + 2O_3 \rightarrow N_2O_5 + 2O_2 \qquad (3)$$

$$N_2O_4 + O_3 \rightarrow N_2O_5 + O_2 \qquad (4)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (5)$$
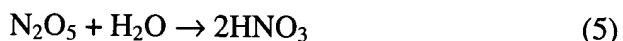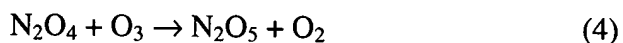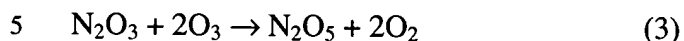
Among these equations, equations (1) – (4) represent the oxidation reactions of NO_x with O_3. Except for the reaction represented by equation (1), all other reactions result in the formation of N_2O_5. However, N_2O_5 may further decompose to form HNO_3 in the presence of water as shown in equation (5).

In order to prevent the problems caused by condensation of water from the sample gas, oxidation reaction chamber 16 should be maintained at a temperature higher than the boiling point of water, preferably at a temperature of $110 \pm 5°C$ using heating device 23, which consists of a heater and insulating material.

By using the temperature setting, the NO_x present in exhaust gas is completely converted to HNO_3, N_2O_5, and NO_2 through the oxidation process described above.

The amount of the O_3 supplied to oxidation reaction chamber 16 should be in the range of 2 - 5 eq of the amount of the NO_x present in the exhaust gas. The capacity of oxidation reaction chamber 16 should be designed to achieve a retention time of the gaseous mixture in the range of 5 – 20 seconds for sufficient reaction. The reaction chamber can be made of stainless steel, titanium, quartz, and glass.

Pyrolysis part

The sample gas, which is obtained from oxidation reaction chamber 16 and contains excess O_3 and oxygen, is introduced through pipeline 17 to pyrolysis reactor 18.

In pyrolysis reactor 18, HNO_3 and N_2O_5 are decomposed to NO_2 through the reactions represented by equations (6) and (8) {it should be (7). – Translator}

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2 \qquad (6)$$

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$$2N_2O_5 \rightarrow 2NO_2 + O_2 \qquad\qquad (7)$$
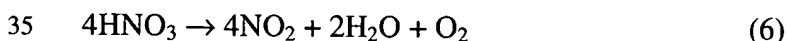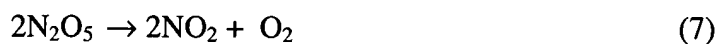
The excess O_3 is also decomposed to O_2 due to heat or the presence of H_2O and NO_2.

5 In order to achieve a smooth and rapid reaction, the reaction temperature should be higher than the boiling point of nitric acid, preferably about 180 - 650°C, maintained by using heating device 24, which consists of a heater and insulating material.

The capacity of pyrolysis reactor 18 and the materials used for the reactor can be the same as
10 those for oxidation reaction chamber 16. However, in order to achieve a high reaction efficiency, a high specific surface area should be used. More specifically, a material with a high specific surface area, such as silica gel, alumina, etc., should be used to fill the reactor.

Measurement part
15 The NO_2-containing sample gas is then sent to gas-sealed sample cell 20 from pyrolysis reactor 18 through pipeline 19.

Gas-sealed sample cell 20 is equipped in the longitudinal direction with a combination of light source 26 and photoelectric tube 27, which is used to determine the concentration of NO_2 using
20 the strong UV absorption band of NO_2. Light source 26 can be, for example, a high-pressure mercury lamp, a tungsten lamp, or a xenon lamp. The signal received by photoelectric tube 27 is sent through amplifier 28 to recorder 29.

Gas-sealed sample cell 20 has a length of 10 m {sic!} for the optical pass. By using a light
25 source with a wavelength of 596 nm, the concentration of the NO_2 present in exhaust gas was determined. Figure 2 shows the relationship between the transmittance (I/I_0) and the concentration. Moreover, the detection limit and measurement accuracy obtained from the experiment are shown in Table 2.

30 Table 2

	Single-beam detection mode	Double-beam detection mode
Lower detection limit	8 ppm	1 ppm
Reading error	± 1 ppm	± 0.1 ppm

After the concentration of NO_x is determined, the sample gas is then released from the system through pipeline 21.

In order to prevent the problems caused by condensation of water from the sample gas, the measurement part, consisting of pipeline 19, gas-sealed sample cell 20, and pipeline 21, is maintained at a temperature higher than the boiling point of water, preferably a temperature of 101[?] - 110°C, using heating device 25, which consists of a heater and insulating material.

Next, another practical example of this invention is explained using Figure 8. This is a practical example using ESR for the detection, so that the quantitative determination of NO_2 is not affected by the H_2O presence in the sample gas.

In the practical example, the procedures for exhaust gas sampling, oxidation with O_3, and pyrolysis of NO_x to NO_2 are the same as in the practical example shown in Figure 1. Then, the NO_2-containing sample gas, maintained at a temperature higher than the boiling point of water, is introduced into the detecting part of ESR 30. The concentration of NO_x is determined by utilizing the Zeeman effect of NO_2.

As shown in Figure 4, when NO_2 is further converted to NO, the concentration of NO_x can be determined by using CLA as a detector for NO.

In the figure, the NO_2-containing sample gas coming from pyrolysis reactor 18 is introduced through pipeline 19 to NO_2-converter 31, where NO_2 is further reduced to NO. The procedures used before pyrolysis reactor 18 are the same as those used in the previous practical example. The NO-containing sample gas coming from NO_2-converter 31 is sent through pipeline 32 to dehydration device 33 using an electronic cooling system to remove the water, which is harmful to the subsequent CLA detector, and then to CLA 34. The concentration of NO_x present in exhaust gas is determined by measuring the concentration of NO in the sample gas.

In this practical example, NO_2-converter 31 can be, for example, a commonly used converter using a M_o-based catalyst operating at a temperature of 350 – 450°C or a stainless steel system {sic!} operating a temperature of 600°C. These systems are sensitive to moisture and may have insufficient reduction for HNO_3. However, the methods for the analysis of nitrogen oxide using these systems are covered by the scope of this invention,

Moreover, NO_2 is converted to NO in NO_2-converter 31. Since NO has very low reactivity towards water, the loss of NO at dehydration device 33 is about 0.8% or lower of the total amount of NO_x present in exhaust gas.

4. Brief description of the drawings

Figure 1 is a flow chart showing a practical example of this invention. Figure 2 shows the results obtained from the determination of NO_x present in an engine exhaust gas using the system described in Figure 1. Figure 3 and Figure 4 are flow charts showing the NO_x measurement parts of two different practical examples of this invention, respectively.

1	Exhaust gas source	3	Dust filter
5	Pump	14	O_3 generator
16	Oxidation reaction chamber	18	Pyrolysis reactor
20	Gas-sealed sample cell		
22, 24	Heating devices		
26	Light source		
27	Photoelectric tube		
30	ESR		

Agent: Takehiko Suzue, patent agent
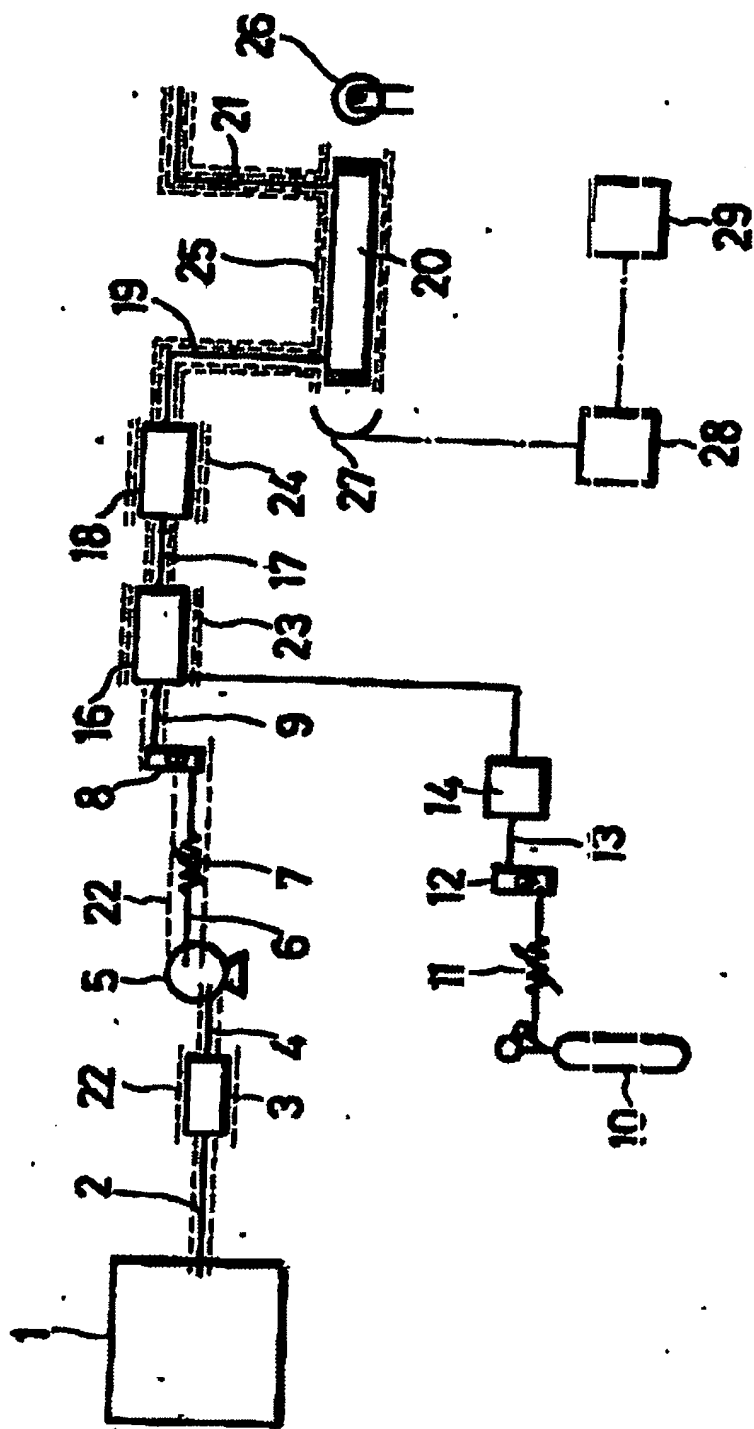
Figure 1

Figure 2

ordinate: Transmittance (I/I_0)

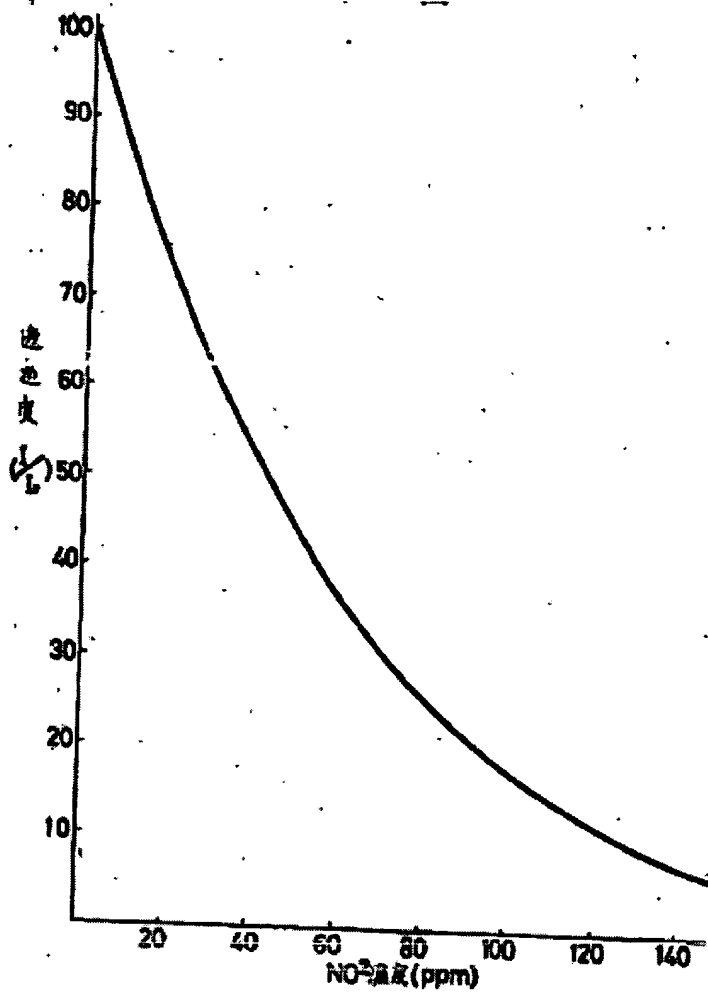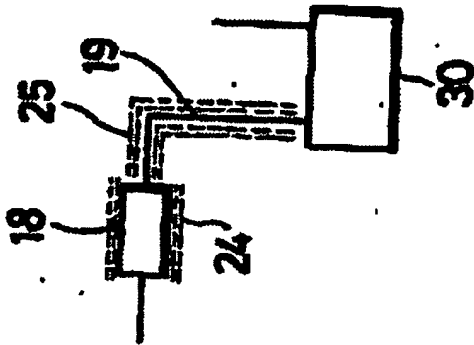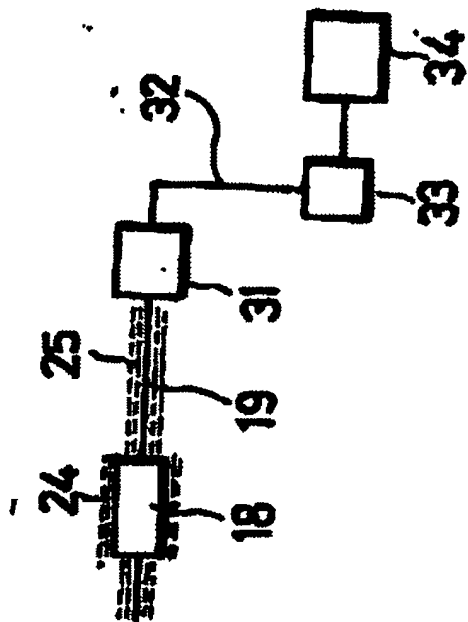abscissa: NO_2 concentration (ppm)

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Figure 3

Figure 4

5   **Amendment**

All corrections have been incorporated into the English version. -- Translator